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A one step synthesis of caprolactam out of cyclohexanone by combined ammoximation and Beckmann rearrangement over Nb-MCM-41 catalysts

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ABSTRACT

Caprolactam was synthesized directly in one step out of cyclohexanone via combined liquid phase ammoximation and Beckmann rearrangement using H_2O_2 and NH_3 in presence of Nb-MCM-41 catalysts and ethanol as solvent. Thereby the Beckmann rearrangement of the oxime to caprolactam occurs simultaneously with the ammoximation of cyclohexanone. Nb-incorporated MCM-41 molecular sieves (Si/Nb-16, 32, 64 and 128) have been synthesized hydrothermally using tetradecyltrimethylammoniumbromide as template in absence of auxiliary organics. Synthesized Nb-MCM-41 samples were characterized using various physical-chemical techniques such as X-ray diffraction, N_2 -physisorption, Atomic Absorption Spectroscopy (ICP-AAS), Thermal Gravimetric Analysis (TGA-DTA), Raman spectroscopy and H_2 -Temperature Programmed Reduction (TPR). All spectroscopic characterization techniques revealed that two types of Nb species are present in the samples. One is tetrahedral coordinated framework Nb species and the other type extra framework Nb_2O_5 species. All these Nb-MCM-41 catalysts were employed to catalyze the ammoximation reaction of cyclohexanone with H_2O_2 and NH_3 and the simultaneously occurring Beckmann rearrangement reaction. The influence of essential reaction parameters such as temperature, NH_3 /cyclohexanone ratios and Si/Nb ratios were investigated. A caprolactam selectivity of 66% was obtained at a cyclohexanone conversion of 7.3% at NH_3 /cyclohexanone molar ratio = 1.5, H_2O_2 : cyclohexanone molar ratio = 1.32 over Nb-MCM-41 (Si/Nb-32) at 80 °C.

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1. Introduction

ϵ -Caprolactam (CL) is an important intermediate monomer for synthesis of Nylon-6 polymers and fibers with a world capacity of about 5.68 mio t/a in 2012 [1]. Industrially, most of the CL is produced in liquid phase by the ammonoximation of cyclohexanone with hydroxylamine in sulfuric acid, followed by the Beckmann rearrangement of the cyclohexanone oxime (CHO) in presence of oleum as catalyst. This process has several disadvantages, such as formation of large amounts of ammonium sulfate as a by-product due to the neutralization of the hazardous sulfuric acid with ammonia, the use of the toxic hydroxylamine and corrosion of the reactors [2,3]. Increase in awareness of environmental protection has led to development of 'clean technology' and green chemistry focusing on minimization of chemical waste and hazardous substances by

using heterogeneous catalysts as a milestone in industrial chemical research [3,4]. Consequently, to suit the current environmental challenges, a new clean processes technology has been developed in the gas phase Beckmann rearrangement reaction over solid acid catalysts [4,5]. In the ϵ -caprolactam production process, several zeolites catalysts have played a crucial role for its production without forming any chemical waste with almost 100% theoretical atom efficiency. Hoelderich et al. have developed specially modified high siliceous B-MFI zeolites which were found to be very active and selective for the Beckmann rearrangement carried out in a fluidized bed reactor with continuous regeneration in a second fluidized bed. The silanol nests and vicinal silanol groups present were found to be the catalytically active sites in partially deboronated B-MFI [3–6]. Recently, Sumitomo Chemical Co. Ltd has commercialized a similar process employing high silica zeolites as catalysts in fluidized bed reactors [7,8]. The further improvement for production of CL was direct ammoximation of cyclohexanone with NH_3 and H_2O_2 catalyzed by TS-1 to form CHO in the first step, followed by its vapor-phase Beckmann rearrangement to CL in the second step [9]. Nevertheless, the gas phase Beckmann rearrangement process

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suffers from high reaction temperature and fast catalyst deactivation. In order to produce CL more efficiently continuous fluidized bed reactor system with continuous regeneration in a second fluidized bed was developed [4]. However, the reaction in these two continuous fluidized bed reactors suffers under high energy consumption.

On the other hand, to overcome these above mentioned problems, synthesis of caprolactam directly from cyclohexanone as starting material by ammoximation in liquid phase conditions using H_2O_2 and NH_3 combined with simultaneous Beckmann rearrangement in a pot type reactor is an alternative route. This route is very interesting consideration from an industrial point of view, because in one stirred tank reactor both ammoximation of cyclohexanone to CHO and CHO rearrangement to CL will take place in presence of bi-functional catalysts. Prasad et al., studied production CL out of cyclohexanone in the presence of NO over TiO_2 , Al_2O_3 - SiO_2 etc. It was found that 37.7% CL selectivity with 46.6% cyclohexanone conversion was observed over Al_2O_3 - SiO_2 catalyst with NH_3 : cyclohexanone = 1.7 (molar ratio), NO: cyclohexanone = 2.9 (molar ratio) at 75 °C reaction temperature [10]. However, using nitrogen oxide as hazardous oxidant is not environmentally benign. Raja et al. studied ammoximation of cyclohexanone to caprolactam over bi-functional molecular sieves catalysts such as Mg-Mn- AlPO_4 -36 using NH_3 and O_2 as an oxidant. Over such bi-functional molecular sieves, the maximum conversion of cyclohexanone 23% and CL selectivity of 45.3% were achieved [11]. Furthermore, this group has reported 68% of cyclohexanone conversion with 78% CL selectivity over $\text{Mn}_{0.02}\text{Mg}_{0.02}\text{Al}_{0.96}\text{PO}_4$ catalyst in presence of air as oxidant [12].

Several efforts have also been undertaken to synthesize CL out of cyclohexanone in presence of nitrosyl sulfuric acid catalyzed by VPO composite catalysts [13], and homogeneous catalysts such as trifluoroacetic acid and hydroxylamine (50 wt% hydroxylamine aqueous solution). In the latter case excellent results have been obtained. The maximum cyclohexanone conversions of 100% and 99% caprolactam selectivity were achieved using acetonitrile as solvent [14]. More recently, F. Aricò et al., investigated synthesis of amides starting of ketones or aldehydes in presence of hydroxylamine hydrochloride which is stable salt as oximation agent and trifluoroacetic acid as catalyst and solvent. The same authors reported highest cyclohexanone conversion of 99% with 84% CL selectivity [15]. Even though, very high cyclohexanone conversion and caprolactam selectivity were achieved, this homogeneously catalyzed liquid phase reaction suffers from many problems of homogeneous catalysis such as separation of the catalyst from the reaction mixture. Other problems are the corrosion of the equipment, toxic solvent, the use of hazardous, toxic nitrosyl sulfuric acid as oxidant and the use of toxic hydroxylamine hydrochloride. In addition the neat and very efficient trifluoroacetic acid/acetonitrile system as homogeneous catalyst and solvent that is not really environmentally benign because TFA is toxic and acetonitrile has delayed toxic effects due to the metabolism to produce HCN already after a short time in the human body.

The present work describes direct one pot production of CL out of cyclohexanone via simultaneous ammoximation and Beckmann rearrangement using H_2O_2 and NH_3 in presence of solid Nb-MCM-41 catalysts. This one pot reaction was studied under various conditions.

2. Experimental

2.1. Synthesis of Nb-MCM-41

Nb incorporated MCM-41 (Si/Nb-16 to 128) molecular sieves synthesis was reported elsewhere [16]. Sodium meta silicate

(ROTH, Germany) and niobium pentachloride (Fluka) were used as sources for silica and niobium. Tetradecyltrimethyl ammonium bromide was used as the structure directing agent (Fluka). The molar composition of the synthesis gels is as follows:

SiO_2 : x NbCl_5 :0.2 TDTAB:0.89 H_2SO_4 :120 H_2O (x varies with Si/Nb ratio).

Four samples with different Si/Nb ratios of 16, 32, 64, and 128 were synthesized. All the samples were dried at 110 °C for 12 h and calcined at 550 °C for 6 h.

2.2. Characterization

Powder X-ray diffraction (XRD) data were recorded on a Siemens Diffractometer (D 5000) operated at 45 KV and 40 mA, using Nickel filtrated $\text{Cu K}\alpha$ radiation with 1.5406 Å between 1.5° and 40° (2 theta), with a scanning speed of 0.02°/min.

Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 Gas Sorption and Porosimetry System. Samples were activated at 300 °C for 3 h in vacuum, and then the adsorption-desorption was conducted by passing nitrogen over the sample, which was kept under liquid nitrogen. Brunauer-Emmett-Teller surface areas of the synthesized catalyst were determined over a relative pressure (P/P_0) range from 0.05 to 0.20. Pore size distributions were calculated from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda method.

Bulk elemental analysis was carried out with Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-AES) on a spectroflame D (Spectro Analytic Instrument).

TGA-DTA measurements were conducted on (NETZCH 209/2/E equipped with a STA-409 controller) with an alumina plate under an air atmosphere (air flow) from ambient to 1000 °C at a heating rate of 10 °C/min.

The Raman spectra of calcined samples were obtained on a (Bruker RFS 100/S) with the 1064 nm line of Nd-YAG laser. Morphological analysis was done with a LEO 1455 EP scanning-electron microscope.

The temperature programmed reduction (TPR) of samples was carried out with TPDRO 1100 apparatus from CE instrument with Thermal Conductive Detector (TCD). First instrument lines were pretreated by passing N_2 (20 ml/min) at 450 °C for 1 h. After cooling to ambient temperature, the nitrogen flow was replaced by 10% H_2 /Ar mixture. The catalyst samples were heated in this atmosphere to 1000 °C at heating rate of 10 °C/min and the flow rate of H_2 /Ar mixture was kept constant at 32 ml/min throughout the experiment.

NH_3 -TPD of samples was measured on TPDRO 1100 apparatus from CE Instrument, with a Thermal Conductive Detector (TCD). Initially, samples were heated at 500 °C under inert gas to remove physisorbed water from the catalysts. Afterwards NH_3 was adsorbed at 100 °C. Subsequently, it was purged with helium for an hour to remove the physisorbed ammonia. The desorption of ammonia was carried out by heating the reactor up to 600 °C. The amount of desorbed ammonia was recorded by a thermal conductive detector (TCD).

2.3. Reaction of cyclohexanone directly to caprolactam

The reactions were carried out in a batch type 3-neck glass (slurry) reactor. The batch reactor system consists of a dry round-bottomed flask equipped with a reflux cooler. The temperature measured in the oil bath was kept stable by a silicon oil bath equipped with a thermostat. The stirring speed was maintained by magnetic stirrer with stirring speed of 1100 rpm. The reactor was charged with required amount of cyclohexanone, ammonia, solvent and catalyst. Reactions were performed using ethanol as solvent and ethanol has taken as 10 wt% of all the reactants mixture.

Table 1
Physical properties of Nb-MCM-41 molecular sieves.

Catalyst	Si/Nb gel ratio	ICP	d ₁₀₀ (Å)	a ₀ (Å)	BET area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)	Wall thickness (Å)
A	16	15.54	33.98	39.24	417	0.28	24.64	14.6
B	32	28.31	49.08	56.67	612	0.26	30.48	26.18
C	64	54.72	41.67	48.12	632	0.36	23.68	24.44
D	128	121.66	38.08	43.97	929	0.94	29.27	14.25

Hydrogen peroxide was introduced continuously for 2 h by slow addition into the reaction mixture under stirring to avoid fast decomposition of H₂O₂. Afterwards the reaction was continued for 2 h under stirring. The reaction was stopped after 4 h and the reactor was cooled down to room temperature. Samples were collected periodically during and after reaction and afterwards centrifuged for separating the catalyst from the reaction mixture. The collected reaction samples were analyzed by Gas Chromatography in order to quantify the conversion and selectivity of the products by internal standard method. The GC analyses were carried out on a Siemens Chromatograph 5890, equipped with a flame ionization detector and a (FS-OV 1701, 50 m) capillary column with methyl undecanoate as internal standard. In the reaction mixture, all products were identified by GC-MS by using GC Varian Star 3400 CX with Varian MS Saturn 3 spectroscopy.

3. Results and discussion

3.1. Chemical and textural analysis

Table 1 exhibits the materials composition based on ICP analysis after calcinations at 500 °C. The data clearly showed that the amount of metal after calcination is close to the expected values. It has been indicated in previous work [17] that the amount of metal incorporated into the framework is mostly depend on the type of silica source used in the synthesis procedure. When sodium silicate was used as the siliceous source, a higher amount of niobium was incorporated in the framework [17].

XRD and BET analysis of the synthesized catalysts revealed that all the catalyst materials have well-ordered hexagonal mesoporous structure of MCM-41 type with one system of pores (around 3 nm pore diameter) and very high surface area (1000 m²/g) [16]. Table 1 summarizes the *d*₁₀₀ spacing and lattice parameter (*a*₀) calculated as per literature from XRD and low-temperature nitrogen adsorption isotherms experiments. It can be seen that, upon introducing the Nb metal into the mesoporous MCM-41, the unit cell parameter calculated by $a_0 = 2d_{100}/\sqrt{3}$ and *d*₍₁₀₀₎ increased. It could be due to the larger ionic radius of Nb⁵⁺ (0.64 Å) and longer Nb–O bond length (1.69 Å). However, a decrease of the unit cell parameter and *d*₍₁₀₀₎ spacing also observed at higher Nb content sample i.e. Si/Nb-16. That could be due to strong interaction of Nb with the inner silica walls and dispersion of high surface Nb concentration. Similar kind of results were also observed in case of other transition metals such as V incorporated mesoporous silica MCM-48 structured material and Nb-MCM-41 molecular sieves [17,18].

According to Zhang et al. [17] the Nb incorporation into framework occurs by two different steps. In first step, the loosely-bonded silica gel has the accessibility for incorporation of heteroatom at room temperature. In second step, Nb is fully condensed into the framework silica under high temperature at hydrothermal conditions. However, in the present investigation we believe that the second mechanism occurred in the synthesis procedure.

Specific surface area, specific pore volume and pore diameter (BJH method) of the calcined materials are presented in Table 1. N₂ isotherm of all calcined samples show type IV

isotherm, (Fig. 3) which is typical for mesoporous materials. The isotherm shows well-defined stages and match with those reported in literature [19]. However, the isotherm of sample Nb-MCM-41(Si/Nb-16) has already lost the characteristic mesoporous solid shape and its surface area decreased sharply to 417 m²/g. The surface area of the catalysts was found in the order Nb-MCM-41(Si/Nb-128) > Nb-MCM-41(Si/Nb-64) > Nb-MCM-41(Si/Nb-32) > Nb-MCM-41(Si/Nb-16). The decrease in the surface area and pore volume with increasing Nb loading can be attributed to the formation of Nb₂O₅ species within the mesopores, which might block the pores of the mesoporous structure. Thus, the incorporation of higher amounts of Nb disrupts the quality of Nb-MCM-41 material. Similarly, pore volume decrease in the same order due to the presence of textural mesoporosity [20].

3.2. TG and DTA results

The results of thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of the as-synthesized Nb-MCM-41(Si/Nb-16–128) catalysts in air are illustrated in Figs. 1 and 2. The data of TG-DTA analysis of Nb-MCM-41 samples exhibited four main steps. The first step, below temperature of 200 °C was associated with physically adsorbed water (2% weight loss). The second part of the TG curve at 200–300 °C was related to the thermal removal of template and contribute to around 35% of total weight loss. This can be attributed to the release of tetradecyltrimethyl ammonium bromide in two ways either by desorption and decomposition, accompanied by an endothermic peak in DTA at 300 °C or by oxidation of tetradecyltrimethyl ammonium bromide. The third part at 400–500 °C was attributed to decomposition and oxidation of remaining template and was accompanied by an exothermic peak in the DTA curve at 450 °C (5% weight loss). Finally, the step above 400 °C can be assigned mainly due to the dehydroxylation of SiOH

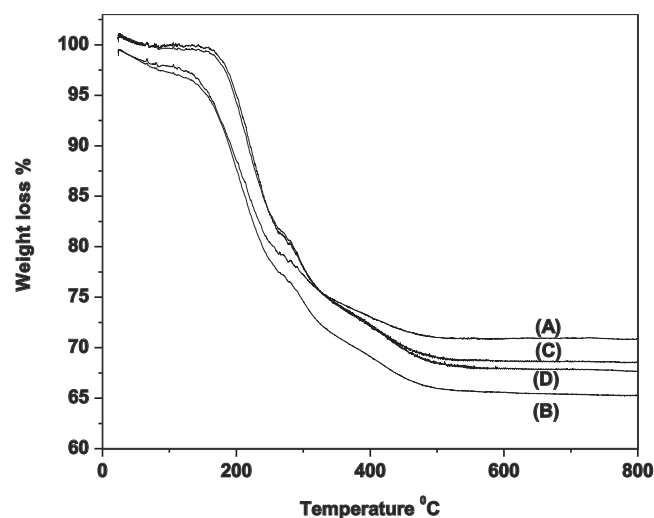


Fig. 1. TGA analysis of Nb-MCM-41 molecular sieves. (A) Si/Nb-16, (B) Si/Nb-32, (C) Si/Nb-64, (D) Si/Nb-128.

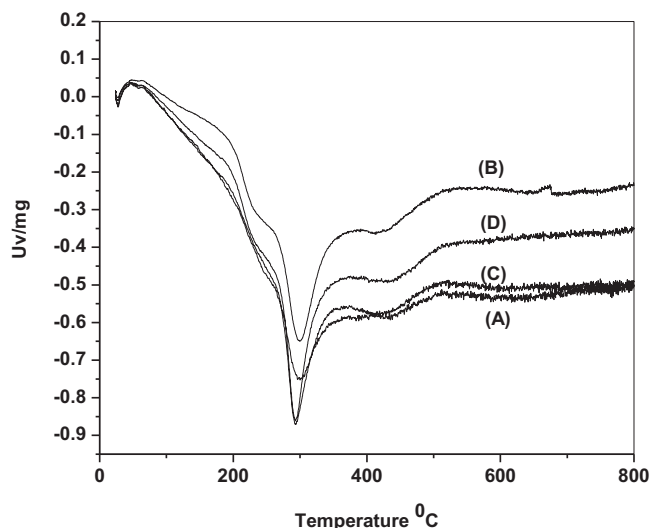


Fig. 2. DTA analysis of Nb-MCM-41 molecular sieves. (A) Si/Nb-16, (B) Si/Nb-32, (C) Si/Nb-64, (D) Si/Nb-128.

groups (<1% weight loss) [20]. The percentages of weight loss were found about 28, 35, 30 and 33% for Nb-MCM-41(Si/Nb-16), Nb-MCM-41(32), Nb-MCM-41(Si/Nb-64) and Nb-MCM-41(Si/Nb-128), respectively.

3.3. Raman spectral analysis

The Raman spectra of calcined Nb-MCM-41 samples with different Si/Nb ratios are presented in Fig. 3. All Nb samples possess strong Raman band at $\sim 990\text{ cm}^{-1}$ which is assigned to Nb=O stretching vibration of isolated NbO_4 species. A weak Raman band could be observed at 810 cm^{-1} which is the characteristic peak of tetrahedral niobium with four oxygen atoms [21,22]. Additional niobium bands in the Raman spectra of these samples observed at 650, ~ 610 , and 470 cm^{-1} are correspond to that of hydrated Nb species similar to that of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ [23]. In addition, it is observed that with increasing the Nb loading (Si/Nb 32 and 16) the intensity of band increased at $607\text{--}650\text{ cm}^{-1}$, characteristic of the stretching mode of Nb–O–Nb polymerized bands [24].

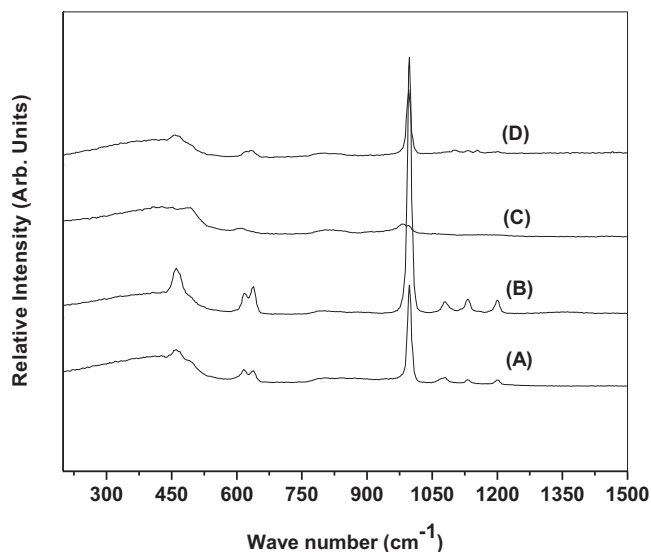


Fig. 3. Raman spectroscopy results of Nb-MCM-41 molecular sieves. (a) Si/Nb-16, (b) Si/Nb-32, (c) Si/Nb-64, (d) Si/Nb-128.

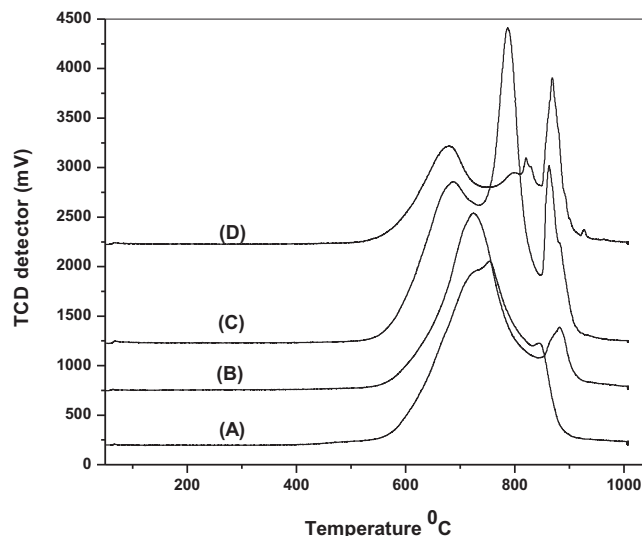


Fig. 4. H_2 -TPR results of Nb-MCM-41 molecular sieves. (a) Si/Nb-16, (b) Si/Nb-32, (c) Si/Nb-64, (d) Si/Nb-128.

Indeed, it shows some Nb_2O_5 species are present at higher Nb loading samples. Additionally, some weak Raman bands appeared at $\sim 1090\text{ cm}^{-1}$, $\sim 1140\text{ cm}^{-1}$ and $\sim 1200\text{ cm}^{-1}$, in case of higher Nb loading samples (Si/Nb 16 and 32), which could be due to the polymeric Nb species. Hence, Raman spectra indicate the presence of two kinds of niobium species are presented in the samples, one is niobium species in the framework, and the other one is agglomerized extra framework niobium species. These results are in resemblance with previously reported results [21].

3.4. H_2 -TPR

The temperature programmed reduction (H_2 -TPR) of calcined Nb-MCM-41 with different Si/Nb ratios are depicted in Fig. 4. The H_2 -TPR profile of different Si/Nb ratios samples shows more than one reduction peak indicating the presence of different niobium species in all the samples. The higher reduction temperature observed for all the samples attribute to the reduction of Nb^{5+} species present within the close vicinity with Si in the framework. The lower temperature reduction peak may be due to the reduction of free Nb^{5+} species present on the outer surface of the framework. The TPR profile of Nb-MCM-41 samples with different Si/Nb ratios clearly indicate that with increasing Nb content, the low temperature reduction peak shifted to high temperature. This may be due to the solid state interaction between siliceous matrix and extra framework niobium species [25]. With decreasing Nb content in the sample, the high temperature reduction peak is more pronounced than in the case of high Nb content samples. These results revealed that the low temperature reduction peak is due to the reduction of extra framework niobium species and reduction peak at high temperature assigned for reduction of framework niobium species. In the high temperature region, various reduction peaks can be observed in case of Si/Nb-64 and 128 samples. These various reduction peaks at high temperature may be due to the reduction of different framework niobium species. In case of Si/Nb-16 sample, reduction peak with shoulder at low temperature (725°C) can be attributed to the reduction of niobium species, which are formed as solid-state interaction between siliceous matrix and extra framework niobium species.

These results are in good agreement with earlier findings of Ziolek et al. [25]. The same authors observed only one sharp reduction peak at low temperature when NbCl_5 was used as the niobium source. Nevertheless, in our present investigation, the reduction

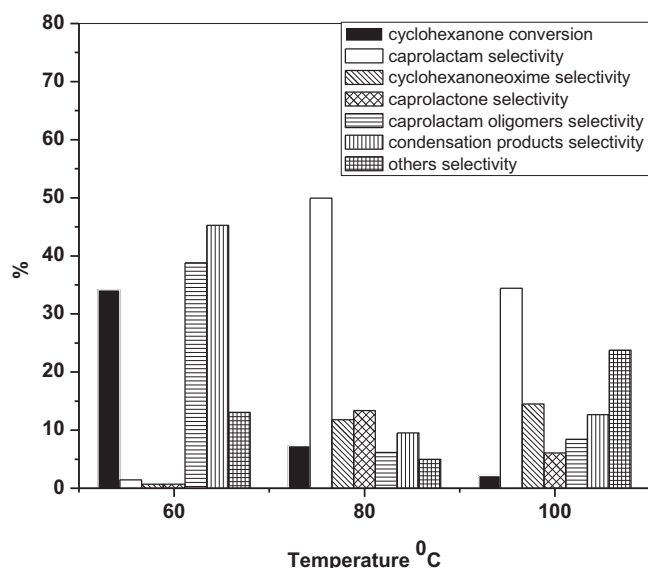


Fig. 5. Effect of reaction temperature over Nb-MCM-41 (Si/Nb-32).

peaks at low temperature and high temperature are pronounced very clearly. From our present results, we can conclude that at low Nb content, samples have more framework niobium species and at high niobium content, samples have more extra framework niobium species. These results are in good agreement with those of Raman spectral analysis.

4. Reaction results over Nb-MCM-41 catalysts in batch reactor

During ammoxidation of cyclohexanone reaction, along with CHO and CL formation other products also have been observed. Some of these by-products were confirmed by GC-MS analysis. These by-products are 2-(1-cyclohexen-1-yl) cyclohexanone, cyclohexylidene-cyclohexanone, and 2-cyclohexenylcyclohexanone which are formed by self-condensation of cyclohexanone in presence of acid catalysts [26–28]. In addition, CL oligomers such as 1-1 peroxydicyclohexylamine was identified by GC-MS in the product mixture. It can be formed by cyclohexanone reaction with hydrogen peroxide and ammonia [29].

Nitrocyclohexane and cyclohexanone oxime might be either derived from consecutive oxidation reactions of cyclohexanone oxime or from side reaction of cyclohexanone. Along with all these by-products aniline was also observed which might have formed from cyclohexanone imine. Cyclohexanoneazine can be derived from the oxidation of the cyclohexanone imine. All reaction by-products are included in the Fig. 5 under the term “other products”. From here onwards “others selectivity” means composition of all these products [30,31].

4.1. Influence of reaction temperature

The effect of reaction temperature of cyclohexanone ammoxidation reactions combined with the simultaneously occurring Beckmann rearrangement over Nb-MCM-41 catalysts was studied at 60 °C, 80 °C, and 100 °C. The results are shown in Fig. 5.

The reaction temperature shows significant influence on the CL selectivity and the product mixture over the Nb-MCM-41 catalyst (Si/Nb-32). As shown in Fig. 5, the conversion of cyclohexanone decreased from 35% to 8% with increasing temperature from 60 °C to 80 °C, whereas the selectivity for CL increased to about 50%. With further increase of the temperature to 100 °C, a rapid

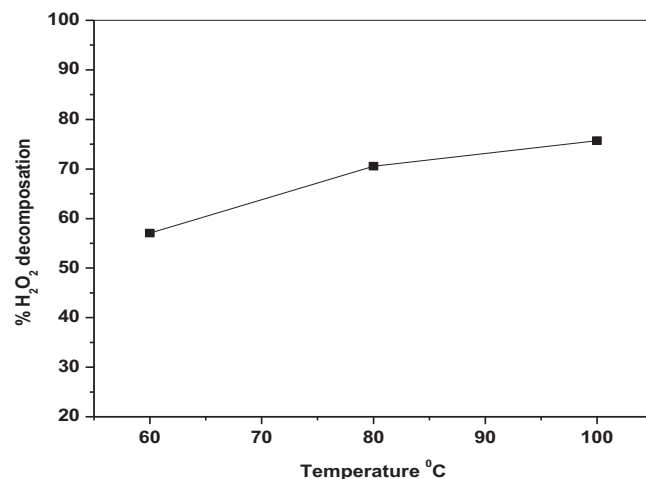


Fig. 6. H₂O₂ decomposition with temperature over Nb-MCM-41 (Si/Nb-32).

decrease of cyclohexanone conversion to 3% and the CL selectivity to 35% was observed. However, at lower reaction temperature the selectivity of the other products (caprolactam oligomers and cyclohexanone condensation products) was higher. “Others selectivity” was decreased with increasing reaction temperature from 60 °C to 80 °C. Furthermore, the CL selectivity also increased with raising the reaction temperature. An increase of CL selectivity with elevating temperature could be due to decomposition of caprolactam oligomers. Furthermore, with increasing the temperature from 80 °C to 100 °C CHO selectivity was increased. The decrease in the conversion of cyclohexanone at high temperature is partially attributed to easier vaporization such as NH₃ and decomposition of hydrogen peroxide. The decomposition of H₂O₂ was measured by iodometric titration method. The decomposition of H₂O₂ with reaction temperature is illustrated in Fig. 6. These results clearly indicate that with increasing reaction temperature from 60 to 100 °C, the H₂O₂ decomposition rate increased from 57 to 75.7%. The formation of cyclohexanone oxime (CHO) as shown in Fig. 5 and also in Table 2 as well as Fig. 7 later on indicates that the procedure to yield caprolactam occurs in a consecutive reaction with CHO as intermediate.

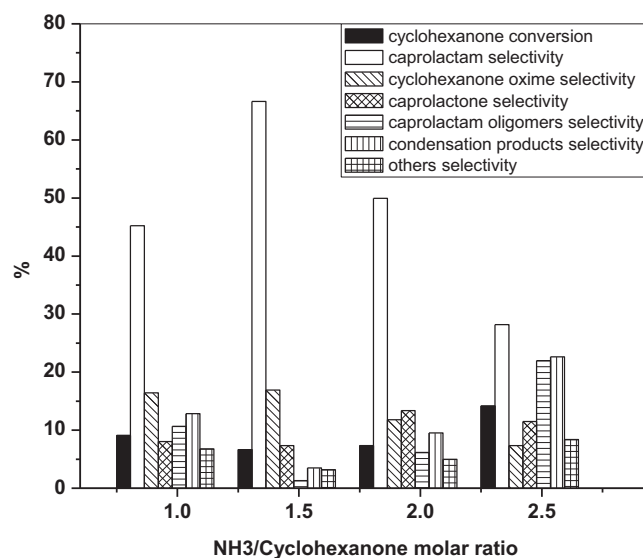


Fig. 7. Effect of NH₃/cyclohexanone molar ratio over Nb-MCM-41 (Si/Nb-32). Conditions: Temp – 80 °C, cat weight – 0.2 g, H₂O₂: cyclohexanone = 1.32 (molar ratio), solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time – 4 h.

Table 2
Effect of Si/Nb ratios over cyclohexanone conversion, CL selectivity and “others selectivity”.

Catal	CHO Conv. %	CL-Sel. %	CHO-Sel%	Capron Seley%	Oligo Sel%	Cond Sel%	Others Sel%
A	30.7	9.1	1.7	2.8	46.5	37.1	2.1
B	6.4	53	13.7	15.9	5.9	7.8	5.6
C	7.3	50	11.8	13.4	6.1	9.5	5
D	8.3	60.4	6.7	9	7.8	10.3	5.8

Conditions: Temp – 80 °C, cat weight – 0.2 g, NH₃: cyclohexanone = 1.94 (molar ratio); H₂O₂: cyclohexanone = 1.32 (molar ratio), solvent-ethanol (10 wt %), stirring speed 900 rpm, reaction time – 4 h

CON. = CONVERSION; SEL = SELECTIVITY; CAPRON = CAPROLACTONE; COND = CONDENSATION.

4.2. Influence Nb content

A series of Nb-MCM-41 catalysts with different Si/Nb ratios (Si/Nb=16–128) were applied for the reaction. The reactions were carried out by maintaining same weight ratio of catalysts, H₂O₂/cyclohexanone and NH₃/cyclohexanone molar ratios. Reaction results are summarized in Table 2.

With decreasing Nb content, the cyclohexanone conversion decreased from 30.7% to 8.3%, however, the CL selectivity increased from 9.1% to 60.4% (Table 2). The maximum CL selectivity of 60.4% was obtained over Nb-MCM-41 (Si/Nb-128) at 8.3% cyclohexanone conversion.

These results can be explained based on the TPD analysis of the catalyst samples [16]. The higher conversions observed with respect to the Si/Nb-16 were in good accordance with the surface acidity of the material as observed by our former studies. The lower cyclohexanone conversions with less Nb can be attributed to the weak acidic sites corresponding to that of the surface hydroxyl groups.

4.3. Effect of NH₃/cyclohexanone molar ratio

The effect of the NH₃/cyclohexanone molar ratios on ammoximation is shown in Fig. 7. With increasing the NH₃ concentration in the reaction mixture from 1.0 to 1.5 molar ratios, the selectivity of CL increased to 65%, but cyclohexanone conversion was only 7%. Further increment of NH₃ concentration from 1.5 to 2.5 the cyclohexanone conversion increased to 15%, but at the same time the selectivity for condensation products and oligomers increased. The high cyclohexanone conversion obtained in an excessive amount of NH₃ was probably due to a partial loss of NH₃ by vaporization. In addition, at high NH₃/cyclohexanone molar ratio, the “selectivity of others” increased. It could be that in presence of an ammonia excess in the reaction mixture, cyclohexanone reacts with ammonia to form a cyclohexanone imine. This imine further reacts with ammonia to lead to higher selectivity of condensation products and others. Also, there is the possibility of blockage of catalytic active acid sites by ammonia may lead to lower cyclohexanone conversion and CL selectivity.

5. Conclusions

The structural and chemical analysis of the various Nb-MCM-41 samples revealed presence of well-ordered mesoporous structure and incorporation of Nb in the framework. N₂ sorption studies revealed that with increasing Nb content, partial loss of mesoporous structure occurred. Raman and H₂-TPR results confirmed that Nb-MCM-41 molecular sieves contain two types of niobium species, one is tetrahedrally coordinated framework Nb species and the other being agglomerized hydrated extra framework Nb₂O₅ species, which are present at higher Nb content samples. The effect of reaction temperature over Nb-MCM-41(Si/Nb-32) catalyst suggests that 80 °C is the optimum temperature for obtaining high caprolactam selectivity. The results

achieved over Nb-MCM-41 catalysts having different Si/Nb ratios demonstrated that the high Nb content samples such as Si/Nb 16 and Si/Nb 32, yield higher activity for the formation of caprolactam. The catalytic activity of these high Nb content Nb-MCM-41 materials is attributed to the increase of acid strength from weak to medium. The effect of NH₃/cyclohexanone ratio over Nb-MCM-41 (Si/Nb-32) catalyst has shown maximum selectivity for caprolactam at 1.5 molar ratio.

Even though the results achieved in the one pot procedure disclosed in the present paper are not competitive with current technologies for caprolactam production at all, it could be demonstrated that the simultaneous oximation of cyclohexanone to cyclohexanone oxime and its consecutive Beckmann rearrangement can be managed in a “one pot”-reaction. Further substantial improvements in reaction conditions and reactor design have been made before such a process will become competitive.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.09.073>.

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